

Exciton-phonon driven Charge-Density-Wave and Superconductivity in TiSe_2

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One of the richest areas of condensed matter physics is the interplay between distinct and competing phases in strongly correlated matter, and the possibility of tuning such systems to a regime where quantum critical fluctuations dominate. Such behaviour can be seen for example in the interplay between antiferromagnetism and superconductivity in the high T_C cuprates and heavy fermion materials [1, 2], and between charge order and superconductivity in materials such as the nearly ferroelectric SrTiO_3 and the charge-density-wave (CDW) ordered transition metal dichalcogenides [3, 4]. It was suggested four decades ago that the suppression of excitonic charge order could also give rise to superconductivity [5, 6], and that excitonic pairing would avoid the temperature limits imposed by phonons, paving the way for room temperature superconductivity. In practice such an exciton-mediated superconducting phase has turned out to be elusive, because phonon softening will typically cause a structural instability to occur before superconductivity has a chance to arise. In this context the very recent discovery of superconductivity in pure TiSe_2 under pressure by Kusmartseva et al. [7] is of great interest, as it hints at the possibility of exciton-mediated superconductivity arising upon the suppression of CDW order in a clean experimental system free of doping-induced disorder or spin ordering. Here we introduce a specific theoretical model to study the possible ways in which CDW and excitonic order can compete, coexist and even cooperate. It is shown that at least in principle the interplay between excitons and phonons can lead to superconductivity before CDW order sets in. By applying the model to the specific case of TiSe_2 we also show that the hitherto elusive mechanism driving the CDW transition in this material is a combination of excitonic and

Jahn-Teller effects, and that furthermore the suppression of the CDW order under pressure is likely to induce an unusual type of superconductivity mediated by combinations of excitonic and phononic fluctuations.

Soon after the explanation of the mechanism of superconductivity by Bardeen, Cooper and Schrieffer [8], it was realised that pairs of electrons could also be stabilised by interactions other than phonon exchange. One such proposed form of alternative ‘pairing glue’ are excitons, or bound particle-hole pairs [5, 6]. It was quickly pointed out that the possibility of excitonic superconductivity would avoid the usual temperature limits imposed by phonons, so that transitions at room temperature or even higher could be envisaged [9]. In practice however, purely excitonic superconductors have not been found to this day. The main reason that this form of pairing remains so elusive is the simple fact that in a real material excitons are never alone. In any material with a lattice phonons are necessarily present and they typically are strongly coupled to the excitons. Promoting exciton formation will therefore usually lead to a strong renormalisation of the phonon spectrum. As the phonons soften in response to the presence of excitons, a lattice instability develops and a charge density wave is formed, thus forestalling the use of the excitons in pair formation.

It is not *a priori* clear however whether or not the detailed interaction between excitons, phonons and electrons allows for superconductivity to arise in principle. The general form of the Hamiltonian for a material which has both excitons and CDW order present is given by:

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{exc}} + \hat{H}_{\text{e-p}}, \quad (1)$$

which includes the bands of non-interacting electrons H_0 , the Coulomb interaction between electrons and holes responsible for creating excitons H_{exc} , and the electron-phonon interaction $H_{\text{e-p}}$. The standard BCS type of superconductivity arises out of the last term, while the purely exciton driven superconductivity is generated by the second term (see figures 1A and B). The combined effect of both of these excitations normally gives rise to CDW formation, but may in principle also lead to superconductivity (figures 1C and D).

The superconductivity recently discovered in pure TiSe₂ under pressure [7] forms a prime candidate for the experimental realization of the exciton plus phonon scenario, as it arises upon the suppression of a CDW order which gives rise to excitonic fluctuations as well

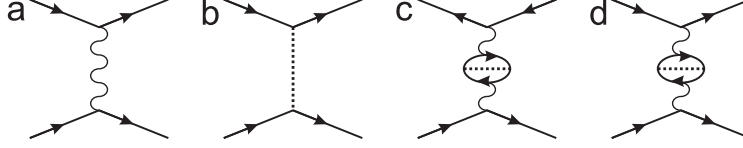


FIG. 1: Feynman diagrams for the different instabilities inherent in the Hamiltonian of eq. (1). **(a)** Cooper pair formation via phonon exchange. **(b)** Cooper pair formation arising from the exciton binding energy. **(c)** CDW formation promoted by electron-hole interaction via renormalised phonons. **(d)** Cooper pair formation via renormalised phonon exchange.

as lattice vibrations. Superconductivity has also been found to arise upon suppression of the CDW by doping, an effect which has been well studied in the intercalated compound Cu_xTiSe_2 [10, 11]. In this case, evidence is mounting that the CDW is destroyed by the imbalance of charge carriers caused by the donation of copper electrons to the Ti bands, leading to conventional superconductivity in which excitons do not play a significant role [12, 13].

Here we present a theoretical model, inspired by TiSe_2 , of the general form of equation (1). We show that exciton formation can support phonon exchange leading to CDW order as well as compete with it, and we show that there is some opportunity for superconductivity to arise via the soft renormalised phonons before CDW order sets in. Applying the model to the specific case of TiSe_2 we suggest that the combined effect of excitons and phonons can explain the long standing riddle of the origin of its commensurate CDW phase as well as drive the superconducting transition.

TiSe_2 has been extensively studied for three decades but is still something of an enigma. In its normal state, it is either a semimetal [14, 15, 16] or a semiconductor [17, 18] with an indirect gap. Many results support each picture, with the only consensus being that the energy gap is a small one of order 100 meV or less. Furthermore, the mechanism driving the transition to the CDW state is still controversial, with the usual Fermi surface nesting picture ruled out [18]. One hypothesis is that a variant of the Jahn-Teller (JT) effect is driving the transition [18, 19, 20, 21, 22], in which a commensurate spatial reconstruction of the lattice lowers the average energy of both the conduction and the valence bands close to the Fermi surface by facilitating partial charge transfer between neighbouring $4p$ and $3d$

orbitals. This could happen through either a lowering of the local bonding state energy, the so-called indirect JT effect described by Whangbo et al. [20], or by causing an alteration in the local crystal field around the Ti atoms, the band-type JT effect introduced by Hughes [19].

The main competing hypothesis is that the transition to a commensurate 2x2x2 state is driven by exciton formation [15, 16, 23, 24] and possibly condensation [25, 26]. The exciton formation is made possible by the paucity of charge carriers in the system and the correspondingly poorly screened Coulomb interaction. With sufficient electron-hole coupling between the valence and conduction bands, the system is unstable to the formation of excitons and deforms with a periodicity governed by the wave-vector connecting them, which in the case of TiSe₂ leads to a doubling of the lattice spacing and backfolding of the conduction band.

Both scenarios are supported by numerical as well as experimental results, but neither can fully explain all the observed effects. For example, electronic band structure calculations which take into account JT effects ([21], and references therein), predict the phonon involved in a JT driven transition to be the so called L_1^- mode. In the exciton driven scenario it is much harder to understand why precisely this mode should become unstable. The nesting of electron and hole pockets in the Fermi surfaces of TiSe₂ is relatively poor, making an incommensurate distortion pattern much more likely. Holt et al. have observed the softening of the L_1^- phonon mode in quasielastic x-ray scattering experiments [27], thus lending support to the idea that a JT effect is important to the CDW transition. On the other hand, evidence that electron-hole coupling must also be an important effect comes for example from ARPES measurements, which show a large transfer of spectral weight to backfolded bands in the CDW phase [24]. Such a large amount of charge transfer cannot be fully accounted for by the JT picture [28].

Recent high resolution ARPES measurements have already led to suggestions that both the excitonic and JT pictures are important [17], and it is with this in mind that we present a model here which draws together the competing JT and excitonic scenarios for CDW formation in TiSe₂ into a coherent picture which is consistent with all experimental findings. The model is based on a tight-binding description of the material which shows that TiSe₂ is best thought of as a network of quasi one-dimensional chains of Ti 3d orbitals weakly

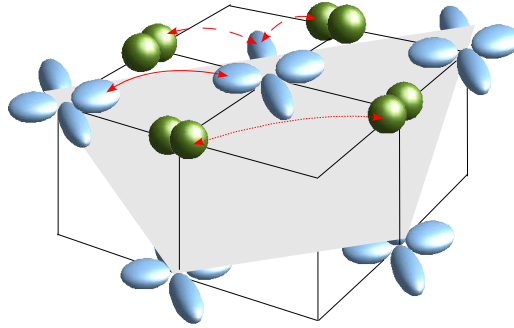


FIG. 2: Overlap integrals relevant to charge-density-wave formation in TiSe_2 . Some of the Se $4p$ and Ti $3d$ orbitals are shown, with the dominant hopping paths between them indicated by red arrows. The upper lines indicate Se-Ti interactions, the middle line shows the Ti-Ti hopping and the lowest line shows the direct Se-Se hopping path. These overlaps, and the ones equivalent by symmetry, represent the only distinct orbital overlap integrals which are not negligibly small in the tight binding description. The shaded plane indicates the orientation of the titanium layer.

coupled together by the surrounding Se $4p$ orbitals [29]. The three dominant interaction pathways making up this network are indicated in figure 2. A complete overview of the calculations leading up to this picture is given in the Supplementary Material.

Because the CDW transition is initiated in what are essentially weakly interacting one-dimensional chains, it should be possible to qualitatively capture the physics of the problem in a (quasi) one-dimensional model system. We will construct such a model based on the parameters of the tight binding fit, and study its phase diagram at the mean field level.

The model system consists of a one-dimensional chain of “Ti” sites, coupled to an adjacent one-dimensional chain of “Se” sites, as in figure 3. The coupling between chains is taken to be a higher order effect and neglected in the present model. The Hamiltonian governing the model will take the form of equation (1). The non-interacting part includes the chemical potential, the bare dispersions along the Ti and Se chains and the hopping between Ti and Se orbitals, all of which are taken directly from the tight binding fit. The exciton binding energy is described as a purely local term which favours electrons and holes to be no further

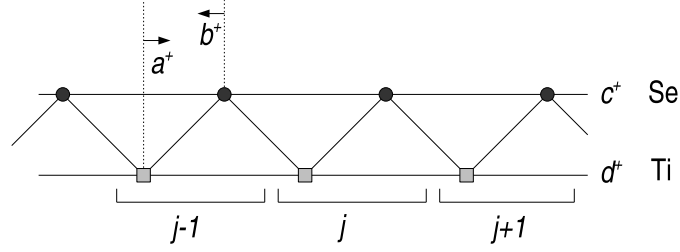


FIG. 3: The quasi one-dimensional chain used as a model for charge-density-wave formation in TiSe_2 . Hoppings from Se to Ti and vice versa are described by combinations of the electronic c and d operators, while lattice deformation is included through the a and b phonon operators.

than one lattice spacing apart:

$$\hat{H}_{\text{exc}} = -V \sum_i \hat{d}_i^\dagger \hat{d}_i \left(1 - \hat{c}_i^\dagger \hat{c}_i\right) + \hat{d}_i^\dagger \hat{d}_i \left(1 - \hat{c}_{i-1}^\dagger \hat{c}_{i-1}\right), \quad (2)$$

where the Se $4p$ -orbitals are occupied by \hat{c}^\dagger creation operators, while the Ti $3d$ -orbitals correspond to the \hat{d}^\dagger operators. The JT effect is then encoded in the electron-phonon term, which couples the orbitals to the phonon operators \hat{a}^\dagger and \hat{b}^\dagger , and their associated distortions, $\hat{X}^a = \hat{a}^\dagger + \hat{a}$ and $\hat{X}^b = \hat{b}^\dagger + \hat{b}$:

$$\hat{H}_{\text{e-p}} = \alpha \sum_i \left[\left(\hat{X}_i^a + \hat{X}_i^b \right) \left(\hat{d}_i^\dagger \hat{c}_i + \hat{c}_i^\dagger \hat{d}_i \right) - \left(\hat{X}_{i+1}^a + \hat{X}_i^b \right) \left(\hat{d}_{i+1}^\dagger \hat{c}_i + \hat{c}_i^\dagger \hat{d}_{i+1} \right) \right]. \quad (3)$$

Before looking at the phase diagram of this model, it should be pointed out that one can straightforwardly obtain a *qualitative* understanding of how exciton-phonon coupling in TiSe_2 can give rise to the observed distortion and charge transfer patterns, based on this picture of weakly crosslinked one-dimensional chains.

Starting from the semiconducting state, consider the effects of hopping from an occupied Se $4p$ -orbital to an empty Ti $3d$ -orbital. For a partial charge transfer the bonding state described by Whangbo et al. is realised [20], and the total energy is lowered due to a gain in kinetic energy. Alternatively, the Ti electron and the Se hole it leaves behind can be said to form an exciton (a bound state with a finite lifetime), in which case the total energy is found to be lowered by the binding energy of this exciton [16]. The energy in both of these pictures can be further lowered by a shortening of the relevant Ti-Se bond, which results in increased orbital overlap (beneficial to the bonding state) as well as an increase in

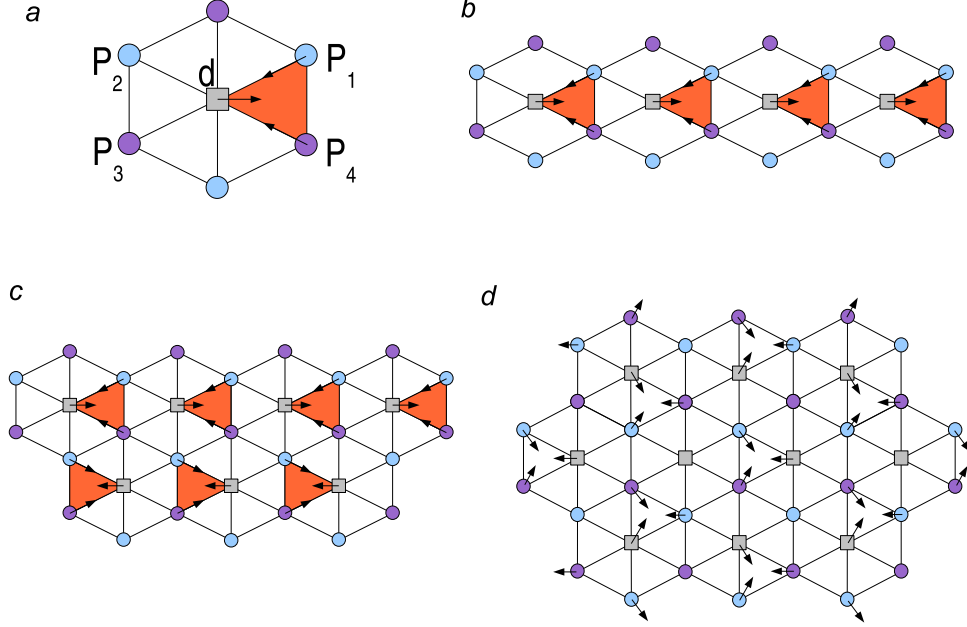


FIG. 4: Mechanism for the observed distortion in TiSe_2 , shown using a c -axis projection of one TiSe_2 layer to illustrate the hopping between Se p -orbitals (light and dark circles) and Ti d -orbitals (grey squares). (a) Hopping between adjacent Se and Ti atoms leading to charge transfer and exciton formation. (b) Deformation pattern along a 1-d ribbon caused by the delocalization of the charge transfer objects in a. (c) Deformation pattern for adjacent 1d ribbons in the charge-density-wave state in TiSe_2 . (d) The deformation pattern that results from the superposition of the distortion pattern in c with its two directional equivalents, a distortion found experimentally in TiSe_2 .

the excitonic binding energy. Focussing on the former influence this effect could be called an indirect JT effect [20] while using the latter it should be described as exciton-phonon coupling [16]. In practice, of course both effects simultaneously contribute to charge being transferred from Se to Ti, and the total energy being lowered.

Further energy can be gained by also transferring some charge from other Se atoms into the partially occupied Ti $3d$ -orbital, as in figure 4a. This process produces an excitonic object spread over two different Se $4p$ orbitals, but sharing the same Ti $3d$ orbital. Alternatively it could be described as a resonating valence bond state occupying these sites.

With the minimal screening in TiSe_2 , the exciton will be tightly bound such that the

electron on the Ti $3d$ orbital cannot escape its one-dimensional hopping path along similar neighbouring Ti orbitals without recombining with a hole on one of the Se $4p$ orbitals. To first order then, the excitons are confined to quasi one-dimensional ribbons in the 2D lattice, as indicated in figure 4b. Simple electrostatic considerations are sufficient to determine that several of these parallel ribbons will orient themselves as shown in figure 4c. This pattern corresponds exactly to the single- q pattern found by Motizuki et al. to be a mode to which the undistorted TiSe_2 is unstable [22]. They also found that the triple- q or L_1^- mode, observed experimentally, was even more unstable. This L_1^- mode corresponds to the superposition of a finite density of all three possible single- q modes (the three ribbon orientations) as shown in figure 4d. It can be easily understood that indeed the L_1^- pattern is energetically favoured over the single- q pattern, by noticing that the environment of a third of the Ti atoms in the L_1^- distorted lattice is made more prismatic, lowering the energy of the lowest Ti $3d$ -orbitals. This is precisely the band-type JT effect of Hughes [19].

Thus all three existing theories are combined into one JT-exciton driven scenario. The exciton formation and indirect JT scenarios effectively combine to cause charge transfer and CDW formation in the quasi one-dimensional Ti chains, which then align themselves in an L_1^- pattern to make full use of the band JT effect, and further lower the overall energy.

Let us now return to the more general model of equations (1)-(3). After introducing mean fields for the lattice distortions ($u = \langle \hat{X}^a + \hat{X}^b \rangle$), the electron densities ($\rho_c = \langle \hat{c}^\dagger \hat{c} \rangle$, $\rho_d = \langle \hat{d}^\dagger \hat{d} \rangle$) and the charge transfer ($\tau = \langle \hat{c}^\dagger \hat{d} + \hat{d}^\dagger \hat{c} \rangle$), the decoupled Hamiltonian can be diagonalised self-consistently and results in a mean field phase diagram. The details of the calculation leading to these diagrams can be found in the Supplementary Material. For the parameter values expected to be relevant to TiSe_2 at ambient pressure, the system sits in a region of the phase diagram that shows roughly the expected behaviour: starting from a high temperature uniform state, the system is found to charge-order upon cooling through a transition temperature. The tendency towards ordering can be enhanced either by increasing the electron hole coupling, or by increasing the exciton binding energy. There is some deviance in the mean field transition temperature scale found here from that seen experimentally, but this is unsurprising given the simplicity of the model. An extension of the model to a three dimensional field theory is expected to resolve this issue and will be discussed elsewhere [30].

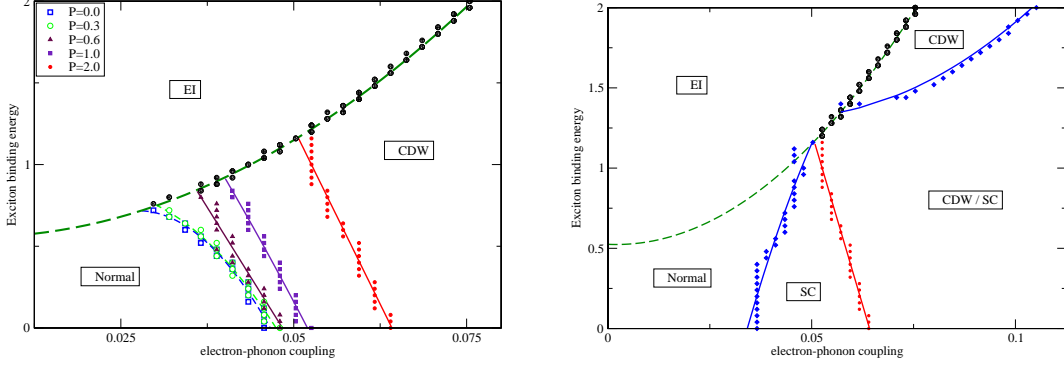


FIG. 5: The mean field phase diagrams of the quasi one dimensional chain of figure 3 for different values of the effective pressure. Lines are included as a guide for the eye only. **Left:** starting from the undistorted phase at the origin, increasing the electron-phonon coupling α/t_0 past a critical value induces a CDW transition, while for any given value of α an increase in the exciton binding energy V/t_0 is seen to enhance the tendency towards CDW formation. At much higher values of V , above the dashed line, the exciton formation saturates the charge transfer and a uniform excitonic insulator is formed. **Right:** the phase diagram at high pressure ($P_{\text{eff}} = 2$), including the superconducting transition.

Apart from describing the region relevant to the situation which is realised in TiSe_2 , the extended phase diagrams produced by this model also highlight the interplay between the different types of order in this system. Some of the diagrams for varying V and α at different values of the reduced effective pressure (defined through $t = t_0(1 + P_{\text{eff}})$ and $t' = t'_0(1 + cP_{\text{eff}})$ with t the Ti-Ti hopping parameter, t' the Ti-Se hopping, and c a constant of order 1) are shown on the left side of figure 5. These diagrams express the changing tendency towards distortion with increasing exciton binding energy or electron-phonon coupling, and clearly demonstrate that while exciton formation enhances the CDW distortion when the exciton binding energy is low, a significantly higher binding energy would lead to the distortion collapsing as an excitonic insulator is formed which exhausts the available charges.

Another feature that is prominently present in this figure, is the difference in the order of the CDW transition upon increasing pressure. The transition starts out being either second order or very weakly first order at $P_{\text{eff}} = 0$, but becomes strongly first order at higher pressures. This behavior is easy to understand in terms of the underlying model: at zero pressure the values of the tight binding parameters are such that the model has

a semiconducting ground state. The energy gained in the formation of a CDW state and the associated folding of the bands is then roughly quadratic in the electron-hole coupling. At high pressures the bandwidth increases and the material becomes semimetallic so that folding the bands gives rise to the opening of a gap, and the energy gain of the CDW formation becomes linear in the coupling.

Having described the CDW formation, we can also include the possibility of finding superconductivity, by introducing the additional order parameters $\phi_{\text{inter}} = \langle \hat{c}^\dagger \hat{d}^\dagger \rangle$ and $\phi_{\text{intra}} = \langle \hat{c}^\dagger \hat{c}^\dagger + \hat{d}^\dagger \hat{d}^\dagger \rangle$ corresponding to inter and intra-band Cooper pairing respectively.

Treated to second order in perturbation theory, the electron-phonon term in the original Hamiltonian, given in equation (3), gives rise to two particle-particle pairing terms, one of each type. The inter-band term has the wrong sign for promoting pair formation though, so the superconductivity caused by the electron phonon coupling term is expected to be predominantly intra-band. The excitonic term in equation (2) also straightforwardly gives rise to an inter-band pairing term, but again it has the wrong sign. Notice that these sign issues arise here only because of the many symmetries of our model system. In general, electron-phonon coupling and exciton binding terms are both expected to contribute to the formation of an inter-band superconducting order parameter [9, 31, 32, 33]. In the simplified model under consideration here, the most likely candidate for causing superconductivity is not directly exciton-mediated pairing, but instead a BCS-like phonon-mediated electron-electron interaction, with the added complexity that the phonons are renormalised by the presence of excitons.

A numerical exploration of phase space shows that within the constraints of our mean-field model, superconductivity can be found in a large region of parameter space, as indicated on the right side of figure 5. As expected, the superconducting pairing is exclusively of the intra-band type with the inter-band order parameter uniformly zero over all of parameter space. As mentioned before however, this is a result of the simplicity of the mean-field model, and it is well possible that in a more detailed theory, taking into account the differences in overlap between one Ti 3*d*-orbital and different neighbouring Se 4*p*-orbitals, also purely excitonic pairing may still appear.

Notice that a large part of the superconducting region in diagram 5 overlaps with the region of CDW order. This does not imply that the two phases actually coexist: the presence

of CDW order indicates that the phonon modes have become unstable in these regions, which implies that the perturbation theory underlying the calculation of the superconducting order parameter is likely to break down. Coexistence cannot be directly ruled out however; Kiss et al. show that in conventional charge ordered materials, including the layered transition metal dichalcogenides, CDW and superconductivity can coexist, and that the superconductivity is in fact boosted at points in k -space connected by the CDW ordering vector [34]. To see whether superconductivity survives in these parts of our phase diagram, a more elaborate treatment is needed, which will be discussed elsewhere [30].

At low values of the exciton binding energy superconductivity in figure 5 is seen to arise before the CDW order sets in. In this region the phonon spectrum is renormalized by the presence of excitons, and these renormalized phonons induce superconductivity in a manner analogous to the conventional BCS type. The renormalization of the phonon spectrum by the presence of excitons directly leads to an enhanced superconducting transition temperature in these regions, as is shown in the right of figure 6. Especially at low pressure, a small excitonic binding energy seems to be beneficial to the superconductivity. Very high binding energies on the other hand always suppress the superconducting order parameter by exhausting the available charges.

The region in figure 5 in which superconductivity gives way to a CDW phase before the excitonic insulator is reached appears above values of the exciton binding energy which are roughly of the order of the bandwidth. This match of energy scales separates the part of phase space in which free, delocalized carriers dominate ($t \gg V$) from the part in which localized excitons are the preferred electronic configuration, and transport occurs via fluctuating valence bonds ($V \gg t$).

Picking out particular values for the parameters in the model, the typical behavior upon altering temperature and effective pressure is shown in the left of figure 6. Starting from the CDW phase, a superconducting dome arises around the point at which the CDW transition reaches zero temperature. In the mean field treatment this superconducting phase extends to high values of the temperature and effective pressure, but taking into account fluctuation effects should reduce the extent of the superconducting phase considerably. The fact that Kusmartseva et al. observe a dome of superconductivity arising around the point where the CDW order disappears suggests the possibility of it being of the type shown in figure 6, in which the excitonic binding energy plays a crucial role in the renormalisation of the phonon

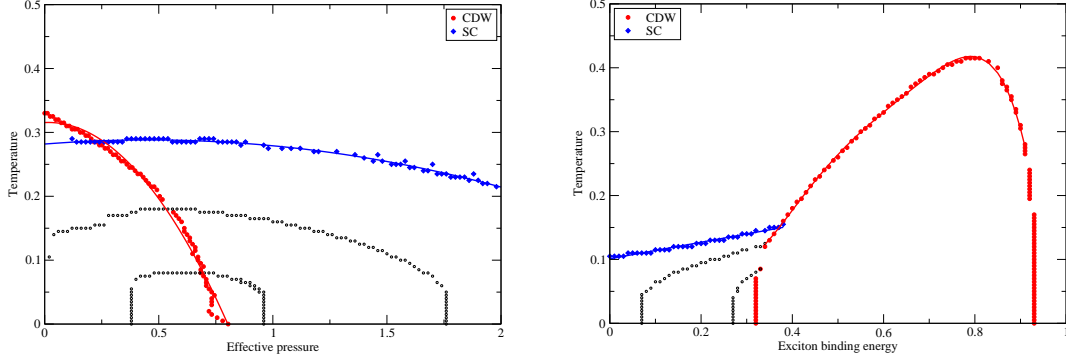


FIG. 6: **Left:** the mean field phase diagram as a function of temperature and effective pressure, for exciton binding energy $V/t_0 = 0.45$ and electron-hole coupling $\alpha/t_0 = 0.043$. The solid lines mark the mean field transition temperatures towards CDW formation and superconductivity. The open circles indicate lines of constant order parameter, which show that the superconducting dome is centered around the point where the CDW ordering temperature reaches zero. **Right:** the phase diagram as a function of temperature and the exciton binding energy at zero pressure and $\alpha/t_0 = 0.043$. Both the superconducting and CDW transition temperatures initially increase with increasing exciton binding energy, but come down again when the exciton formation depletes the available charges.

spectrum, enabling superconductivity to occur just before the lattice becomes unstable.

Further experimental and theoretical investigations are necessary to clarify the extent of the relative contributions of excitons and phonons to the superconducting order parameter in TiSe_2 . One way in which this might be done is to use the folding of the bands in the CDW region. The reconstruction of the Brillouin zone brings the charge transfer processes which are normally inaccessible at high wavevectors and low energies back to the region of low wavevectors. It may thus be possible to optically probe this charge channel on the CDW ordered side close to the transition and directly measure the strength of either effect.

In conclusion, we have presented a simple quasi one-dimensional model in which the interplay between electron-phonon coupling and exciton formation can be studied. The mean field phase diagram of this model shows that the phonon renormalisation caused by the presence of excitons can either assist the formation of charge density wave order (at low binding energy) or oppose it (at high energy). Likewise, the renormalised phonons may be more or

less prone to cause superconductivity depending on where in the phase diagram they occur. From the mean field treatment it is not yet clear whether superconductivity and charge density wave order can coexist in any of these regions. However, there are at least some regions in phase space in which the balance between exciton binding energy and electron-hole coupling can cause superconductivity before the onset of CDW order.

Applying our model to the specific case of TiSe_2 , we argue that existing models relying solely on either excitons or on Jahn-Teller effects to explain the CDW transition in 1T- TiSe_2 are incomplete, and that excitons, orbitals and phonons are all necessary ingredients in a description of the CDW phase. A qualitative understanding of this Jahn-Teller/exciton driven scenario follows directly from the realisation that the main features of the band structure of TiSe_2 result from what are essentially weakly coupled one-dimensional chains of Ti $3d$ -orbitals. Our mean field treatment of the quasi one-dimensional model incorporating the coupling between exciton formation and Jahn-Teller effects can reproduce the experimentally determined phase diagram using parameters taken from a tight-binding fit to LDA calculations and from the experimental literature. In this context, the observation of a dome of superconductivity around the zero temperature CDW transition suggests that the pairing there is due to phonons which are strongly renormalized by the presence of excitons.

The combined Jahn-Teller/exciton scenario has resolved the long-standing question of how the observed L_1^- CDW pattern in 1T- TiSe_2 is formed, and provides a platform for explaining the nature of the superconductivity which appears as the CDW order is suppressed by pressure. The physics around the potential quantum critical point in this system will be treated in more detail in a subsequent work, but it is evident from the simplified model studied here that fluctuations corresponding to the suppression of the CDW are essential for the emergence of superconductivity in this system. The precise extent of excitonic involvement in these fluctuations and the superconducting state may be resolved in future optic experiments close to the transition, but it is clear from the present considerations that excitons as well as electron-phonon coupling have an important role to play in both ordered phases of TiSe_2 .

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Competing financial interests

The authors have no competing financial interests.

Supplementary Material

I. THE TIGHT BINDING DESCRIPTION

Details of the tight binding fitting procedure can be found elsewhere [29], but are included here also for completeness.

TiSe₂ is a layered material with hexagonal layers of Ti sandwiched by octahedrally coordinated Se atoms, the so-called 1T-polytype for transition metal dichalcogenides. The layers are separated from each other by a Van der Waal's gap, which allows us to neglect the effects of inter-layer coupling to a first approximation. The octahedral coordination of the Ti atoms splits its d-shell electrons into a set of high energy e_g orbitals and low lying, degenerate t_{2g} orbitals, all of which would be empty in a purely semiconducting ground state. Because the e_g orbitals are much higher in energy than the t_{2g} , we will focus on the latter and only consider the effects of charge transfer between them and the surrounding Se $4p$ -orbitals. The tight binding Hamiltonian can then be written as:

$$\begin{aligned} \hat{H} = & \sum_{i,\alpha} \frac{\Delta}{2} \left(\hat{d}_{i,\alpha}^\dagger \hat{d}_{i,\alpha} - \hat{p}_{1i,\alpha}^\dagger \hat{p}_{1i,\alpha} - \hat{p}_{2i,\alpha}^\dagger \hat{p}_{2i,\alpha} \right) \\ & + \sum_{\langle i,j \rangle, \alpha, \beta} \left(t_{\alpha, \beta, i-j}^{dd} \hat{d}_{i,\alpha}^\dagger \hat{d}_{j,\beta} + t_{\alpha, \beta, i-j}^{pp} \left[\hat{p}_{1i,\alpha}^\dagger \hat{p}_{1j,\beta} + \hat{p}_{2i,\alpha}^\dagger \hat{p}_{2j,\beta} \right] \right) \\ & + \sum_{\langle i,j \rangle, \alpha, \beta} \left(t_{\alpha, \beta, i-j}^{pd} \left[\hat{d}_{i,\alpha}^\dagger \hat{p}_{1j,\beta} + \hat{d}_{i,\alpha}^\dagger \hat{p}_{2j,\beta} + H.c. \right] + t_{\alpha, \beta, i-j}^{pp} \left[\hat{p}_{1i,\alpha}^\dagger \hat{p}_{2j,\beta} + H.c. \right] \right) \end{aligned} \quad (4)$$

Here \hat{d}_i^\dagger , \hat{p}_{1i}^\dagger and \hat{p}_{2i}^\dagger create electrons on the Ti, the upper Se and the lower Se atom respectively in the unit cell centered at \vec{R}_i . The labels α and β run over all possible orientations of the Ti t_{2g} and Se p -orbitals and $\langle i, j \rangle$ denotes neighbouring sites both within and between unit cells. The difference in chemical potential between the orbitals is given by Δ , while all the different hopping pathways are included in the matrices t^{dd} , t^{pd} , and t^{pp} .

Many of the interactions between neighbouring orbitals are (nearly) zero due to the symmetry of the crystal lattice. The remaining entries can be expressed in terms of Slater-Koster integrals.[35] Ignoring the weakest of these integrals,[36] there remain only seven different non-zero overlaps which are not equivalent under symmetry transformations (see figure 7). Writing these seven overlap integrals in terms of only five relevant Slater-Koster integrals and taking into account the chemical potential difference between the Ti and Se sites, we

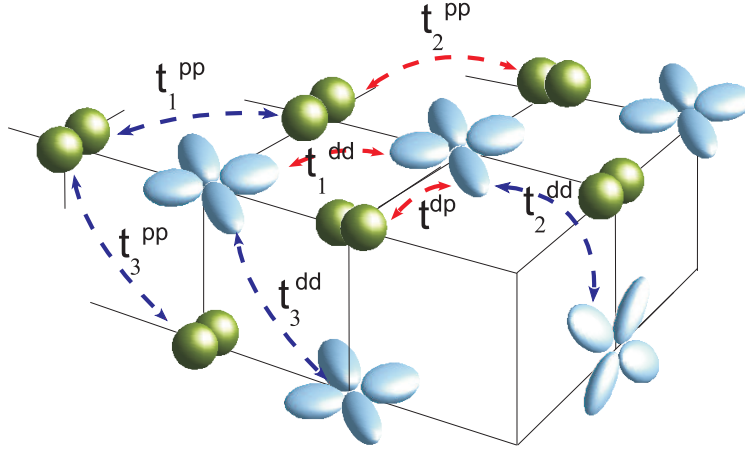


FIG. 7: The seven inequivalent hopping pathways used in the tight binding description. All other overlap integrals are either zero by symmetry or expected to be negligibly small.

can transform the Hamiltonian to momentum space and obtain the band structure for this model by diagonalizing the resulting 9×9 matrix. By adjusting the values of the Slater-Koster integrals the tight binding bands can then be fit to the band structures obtained in earlier (LDA) calculations.[13, 23, 37] The resulting fits are shown in figure 8.

As can be seen from the figures, our tight binding results are in good qualitative agreement with the earlier results: the energies at the high symmetry points approach the expected values, and there is a clear qualitative agreement in the shape of the bands. The values of the parameters that give the optimal fit suggest that three Slater-Koster integrals in particular dominate the behaviour of the bands. In fact, setting the other overlap integrals identical to zero and repeating the fitting procedure with only Δ , $(dd\sigma)$, $(pp\sigma)$ and $(pd\pi)$ as fitting parameters results in fits which are very similar to the ones shown in figure 8 both in appearance and in their closeness to the LDA results. This observation leads us to the conclusion that only three hopping pathways contribute significantly to the behaviour of charges close to the Fermi energy in TiSe_2 . These three pathways are shown in red in figure 7, from which it becomes clear that they constitute a network of chains of Ti $3d$ -orbitals, connected to other chains only via the Se p -orbitals.

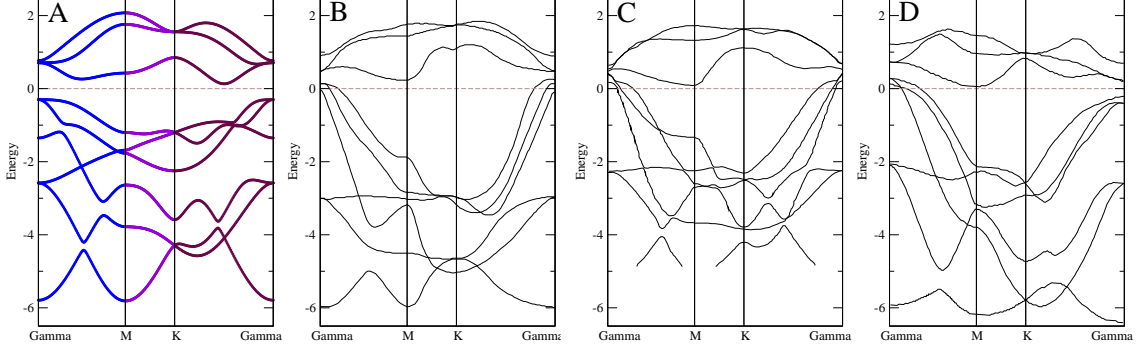


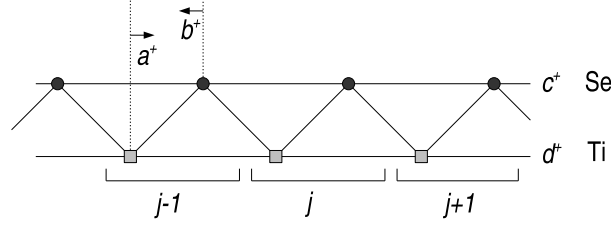
FIG. 8: Comparison of the tight binding band structures with earlier calculations. Figure A shows the results of our calculations with parameters which give the best overall agreement with all of the previous results. Figure B compares the result to the LDA calculations of Zunger and Freeman [23], figure C to the DFT results of Jishi et al. [13] and figure D to the 23-parameter tight binding calculations of Yoshida et al. [37]. The values for the three most important Slater-Koster integrals used in these fits are: $(dd\sigma) = -0.75$, $(pp\sigma) = 0.6$ and $(pd\pi) = 1.1$.

II. THE DOUBLE CHAIN MODEL

To study the effects of electron-phonon coupling and exciton formation in TiSe_2 , we use a simplified model based on the observation that only orbital overlaps along weakly coupled one-dimensional titanium chains, and with their adjacent selenium orbitals, contribute significantly to the tight-binding band structure. The model thus consists of two coupled chains, one representing the Se $4p$ -orbitals and the other the Ti $3d$ -orbitals. Both the difference in chemical potential between these sites and the overlap integrals connecting them are taken directly from the tight binding results. Together with the phonon energy (whose value is taken from experiment), they constitute the bare potential and kinetic energy terms of the model:

$$\begin{aligned} \hat{H}_0 = & \hbar\omega \sum_i \left(\hat{a}_i^\dagger \hat{a}_i + \hat{b}_i^\dagger \hat{b}_i \right) + \frac{\Delta}{2} \sum_i (\hat{d}_i^\dagger \hat{d}_i - \hat{c}_i^\dagger \hat{c}_i) \\ & + \frac{1}{2}t \sum_i (\hat{d}_i^\dagger \hat{d}_{i+1} + \hat{c}_i^\dagger \hat{c}_{i+1} + H.c.) + t' \sum_i (\hat{d}_i^\dagger \hat{c}_i + \hat{d}_{i+1}^\dagger \hat{c}_i + H.c.), \end{aligned} \quad (5)$$

where i labels unit cells with one \hat{c}^\dagger (Se) and one \hat{d}^\dagger (Ti) atom, as in figure 9. The positions of the atoms within the unit cell can be modified by the presence of phonons, indicated with \hat{a}^\dagger and \hat{b}^\dagger . The sign convention in the definition of these phonons is chosen such that

FIG. 9: Simplified double chain model of TiSe_2

$\hat{X}^a \equiv \sqrt{\hbar/(2m\omega a^2)}(\hat{a}^\dagger + \hat{a})$ indicates the displacement of a Ti atom to the right, while $\hat{X}^b \equiv \sqrt{\hbar/(2m\omega a^2)}(\hat{b}^\dagger + \hat{b})$ represents a Se atom shifted to the left.

Electrons and phonons will be coupled in the model through the dependence of the overlap integrals on the distance between atomic orbitals. The change in overlap in the presence of a distortion is given by:

$$\hat{H}_{\text{e-p}} = \alpha \sum_i (\hat{X}_i^a + \hat{X}_i^b)(\hat{d}_i^\dagger \hat{c}_i + \hat{c}_i^\dagger \hat{d}_i) - (\hat{X}_{i+1}^a + \hat{X}_i^b)(\hat{d}_{i+1}^\dagger \hat{c}_i + \hat{c}_i^\dagger \hat{d}_{i+1}). \quad (6)$$

Notice that this coupling term includes an effective description of the indirect Jahn Teller effect of Whangbo et al.[20] Additionally, we will describe the exciton binding energy in our model by a term lowering the energy of Se holes in the presence of a neighbouring Ti electron. This extremely local form of the binding energy is appropriate in a model for TiSe_2 , in which the Coulomb interaction is poorly screened, and excitons are expected to be tightly bound:

$$\hat{H}_{\text{exc}} = -V \sum_i (\hat{d}_i^\dagger \hat{d}_i (1 - \hat{c}_i^\dagger \hat{c}_i) + \hat{d}_{i+1}^\dagger \hat{d}_{i+1} (1 - \hat{c}_i^\dagger \hat{c}_i)). \quad (7)$$

The physics described in this model will depend on the interplay between three effects: exciton formation, electron-phonon coupling and superconductivity. All of these can be studied at the mean-field level using the above contributions to the Hamiltonian.

A. A Mean Field Treatment of the CDW Transition

To first understand the interplay between exciton formation and electron-phonon coupling without the added complications of superconductivity, let us start by introducing only mean fields which conserve particle number. These are the average electron density on the Ti and Se sites, $\langle \hat{d}_i^\dagger \hat{d}_i \rangle$ and $\langle \hat{c}_i^\dagger \hat{c}_i \rangle$; the charge transfer between Ti and Se sites both within and

between unit cells, $\langle \hat{c}_i^\dagger \hat{d}_i \rangle$ and $\langle \hat{c}_i^\dagger \hat{d}_{i+1} \rangle$; and the displacements of the Ti and Se atoms within each unit cell, $\langle \hat{X}_i^a \rangle$ and $\langle \hat{X}_i^b \rangle$. If we name these mean field expectation values ρ_d , ρ_c , τ_{in} , τ_{out} , u_a and u_b respectively, then the fully decoupled Hamiltonian describing the charge density wave formation in the normal (non-superconducting) phase of the system is given by:

$$\begin{aligned} \hat{H} = & \sum_k \left\{ \hbar\omega (\hat{a}_k^\dagger \hat{a}_k + \hat{b}_k^\dagger \hat{b}_k) \right\} + 2\alpha \text{Re}(\tau_{in} - \tau_{out}) \sqrt{N} \left[\hat{a}_{k=0}^\dagger + \hat{a}_{k=0} + \hat{b}_{k=0}^\dagger + \hat{b}_{k=0} \right] \quad (8) \\ & + \sum_k \left\{ \hat{c}_k^\dagger \hat{c}_k \left[t \cos(ka) - \frac{\Delta}{2} + 2V\rho_d \right] + \hat{d}_k^\dagger \hat{d}_k \left[t \cos(ka) + \frac{\Delta}{2} + 2V(\rho_c - 1) \right] \right. \\ & \quad + \hat{d}_k^\dagger \hat{c}_k \left[t'(1 + e^{ika}) + \alpha(u_a + u_b)(1 - e^{ika}) - V(\tau_{in} + e^{ika}\tau_{out}) \right] \\ & \quad \left. + \hat{c}_k^\dagger \hat{d}_k \left[t'(1 + e^{-ika}) + \alpha(u_a + u_b)(1 - e^{-ika}) - V(\tau_{in}^* + e^{-ika}\tau_{out}^*) \right] \right\}. \end{aligned}$$

Notice that in the Bosonic part of this Hamiltonian, only the $k = 0$ components of the displacement operators show up, because we require the mean field solution to be translationally invariant. This form of the Hamiltonian can be straightforwardly diagonalized by introducing shifted operators for the phonon modes and employing a Bogoliubov transformation to solve the Fermionic part. Physically, this corresponds to a renormalization of the phonon spectrum (at $k = 0$) due to the charge transfer from Se to Ti sites caused by exciton formation and the formation of valence bonds, while simultaneously the electronic spectrum is renormalized due to both the presence of lattice distortions, and the interplay between exciton formation and valence bonding.

After filling up the diagonalized electronic states using the Fermi-Dirac distribution, the values of the mean fields can be found self-consistently. The resulting phase diagrams for the variation of two of the parameters is shown in figure 10. For the values of the parameters given by those of the tight binding fit and using straightforward estimates of the parameters α and V based on experimental findings, we indeed find ourselves in a region of the phase diagram with a finite temperature charge-density wave transition. The temperature scales in our model are not expected to correspond quantitatively to the transition temperature observed in TiSe₂ because of the highly simplified nature of the model. The qualitative physics driving the transition however, is expected to be captured in the present model. In particular, the shape of the phase diagram varying α and V clearly shows that the presence of an electron-phonon coupling stemming from the indirect Jahn-Teller effect favours the formation of charge density waves (and their associated lattice distortions). At the same

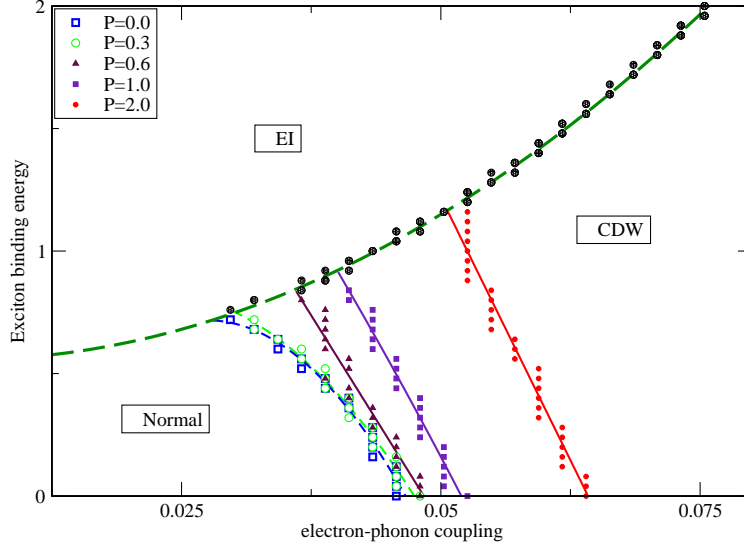


FIG. 10: The mean field phase diagrams for the double chain model for different values of the effective pressure, with superconductivity explicitly suppressed. Both electron-phonon coupling (Jahn-Teller effects) and exciton formation can be seen to play a role in the transition to the CDW phase.

time it is also clear though, that the presence of an excitonic binding energy greatly assists the generation of charge transfer and the formation of density modulations. For the area of phase space relevant to the description of TiSe_2 , both of these effects play an important role. The CDW transition in the real material is thus expected to be driven by a combination of excitonic and Jahn-Teller effects, as anticipated in our qualitative description based on the presence of quasi one-dimensional chains.

B. A Mean Field Treatment of the SC Transition

Having found a description corresponding to the charge density wave transition in the normal state of TiSe_2 which takes into account both the effect of indirect Jahn Teller coupling and of exciton formation, we can now introduce mean fields that do not conserve particle number to see if superconductivity arises as the CDW order is suppressed. The expectation is that the suppression of the CDW transition towards a quantum critical point (f.e. due to the application of pressure) will give rise to soft phonon modes due to the presence of slow charge fluctuations, which can be employed to assist in the formation of Cooper pairs. As in

the description of the normal state, the phonon operators featuring in this transition will be renormalized both by the presence of an indirect Jahn Teller effect and due to the formation of excitons. To account for Cooper pair formation via the phonons in our mean field model, we expand the electron-phonon coupling term to second order in α/ω , yielding the terms:

$$\hat{H}'_{\text{e-p}} = \frac{\alpha^2}{\omega} \frac{1}{N} \sum_{k,q} \left\{ 4(1 - e^{ik})(1 - e^{-iq}) \hat{c}_q^\dagger \hat{d}_{-q}^\dagger \hat{d}_{-k} \hat{c}_k - [(1 - e^{ik})(1 - e^{-ik}) + (1 - e^{iq})(1 - e^{-iq})] \hat{c}_k^\dagger \hat{c}_{-k}^\dagger \hat{d}_{-q} \hat{d}_q + H.c. \right\}. \quad (9)$$

These terms will be decoupled using only the mean fields for the superconducting order parameters $\langle \hat{c}_k^\dagger \hat{c}_{-k}^\dagger \rangle$, $\langle \hat{d}_k^\dagger \hat{d}_{-k}^\dagger \rangle$ and $\langle \hat{c}_k^\dagger \hat{d}_{-k}^\dagger \rangle$. In addition we will also keep the original, full electron-phonon interaction term, but decouple that one using only the particle-conserving mean fields. This way we can keep the full renormalization of the phonon spectrum due to Jahn Teller effects, while also treating the Cooper pair formation caused by the (renormalized) phonons appearing in the second order perturbation theory.

The exciton binding energy of equation (7) will directly give rise to a mean field pairing interaction similar to the first term in $\hat{H}'_{\text{e-p}}$, in addition to the effects discussed in the last section. Notice that both this direct excitonic pairing term and the first phononic pairing term in $\hat{H}'_{\text{e-p}}$ produce inter-band Cooper pairs consisting of one electron in the Se band and one in the Ti band. These terms all come with a sign that does not seem to favour the formation of pairs. Notice however that this is largely due to the many artificial symmetries imposed on our simplified model description. In a more general treatment, taking into account the difference in orbital overlap between different orientations of the Ti 3d and the two spatially distinct Se 4p-orbitals as well as the interchain coupling, these pathologies are expected to disappear. In that case it is not unlikely that inter-band pairing due to direct exciton exchange will be favoured for at least some values of the Cooper pair momentum. Likewise, inter-band pairing of renormalized electrons due to the exchange phonons may well appear in a more general model. Given the present simplified one-dimensional model though, superconductivity is expected only in the intra-band channels described by the last term of equation (9). Notice that the different species of intra-band Cooper pairs (consisting of either Se or Ti electrons) are coupled through this term.

The fully decoupled mean field Hamiltonian can be diagonalized in much the same way as was done for the description of the normal state, with the difference that one now needs

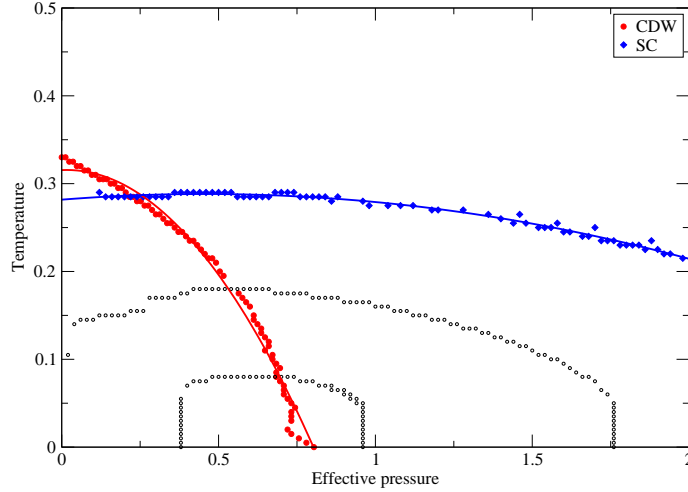


FIG. 11: The mean field phase diagram for the double chain model. A superconducting dome is seen to arise around the point at which the CDW transition temperature is tuned to zero temperature. The solid lines mark the mean field transition temperatures towards CDW formation and superconductivity. The open circles indicate lines of constant order parameter, which show that the superconducting dome is centered around the point where the CDW ordering temperature reaches zero.

to introduce a chemical potential for the electrons and use an extended Bogoliubov transformation to include particle-particle as well as particle-hole channels. Solving the resulting equations self-consistently leads to the phase diagram shown in figure 11. This temperature-pressure phase diagram obtained by taking the tight binding results as zero pressure values of t' and t , and increasing them proportionally with pressure, shows the typical dome shape characteristic of superconducting order arising around a quantum critical point. Varying the exciton binding energy and the bare electron phonon coupling gives rise to changes in the size of the dome. The presence of some exciton binding certainly helps to stabilize the superconducting state, making the dome wider, but having values of V which are too high is detrimental for the superconductivity as all electrons will be bound up in localized, electrically neutral particle-hole pairs. To find the extent to which exciton formation assists or opposes Cooper pair formation in TiSe_2 , we need a more realistic model taking into account interchain coupling, orbital orientations and fluctuations. A field theoretical approach describing these effects and their influence on the appearance of superconducting order in TiSe_2 will be published elsewhere.[30]

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- [1] Waldram, J. R. *Superconductivity of Metals and Cuprates*. Taylor & Francis, (1996).
 - [2] Mathur, N. D., Grosche, F. M., Julian, S. R., Walker, I. R., Freye, D. M., Haselwimmer, R. K. W., and Lonzarich, G. G. Magnetically mediated superconductivity in heavy fermion compounds. *Nature* **394**, 39–43, July (1998).
 - [3] Schooley, J. F., Hosler, W. R., Ambler, E., Becker, J. H., Cohen, M. L., and Koonce, C. S. Dependence of the superconducting transition temperature on carrier concentration in semiconducting SrTiO₃. *Phys. Rev. Lett.* **14**(9), 305–307, Mar (1965).
 - [4] Sipos, B., Kusmartseva, A. F., Akrap, A., Berger, H., Forro, L., and Tutis, E. From Mott state to superconductivity in 1T-TaS₂. *Nat. Mater.* **7**(12), 960–965, December (2008).
 - [5] Little, W. A. Possibility of Synthesizing an Organic Superconductor. *Phys. Rev.* **134**(6A), A1416–A1424, June (1964).
 - [6] Ginzburg, V. L. . *Sov. Phys. JETP* **20**, 1549, (1965).
 - [7] Kusmartseva, A. Pressure induced superconductivity in pristine 1T-TiSe₂. *Workshop on Critical Fluctuations in Spin and Charge Systems*, Cambridge (UK), 13 November 2008.
 - [8] Bardeen, J., Cooper, L. N., and Schrieffer, J. R. Theory of Superconductivity. *Phys. Rev.* **108**(5), 1175–1204, December (1957).
 - [9] Dolgov, O.V., and Maksimov, E.G. Transition temperature of strong coupling superconductors. *Sov. Phys. Usp.* **25**(9), 688–703, Sept (1982).
 - [10] Morosan, E., Zandbergen, H. W., Dennis, B. S., Bos, J. W. G., Onose, Y., Klimczuk, T., Ramirez, A. P., Ong, N. P., and Cava, R. J. Superconductivity in Cu_xTiSe₂. *Nat. Phys.* **2**(8), 544–550, August (2006).
 - [11] Morosan, E., Li, L., Ong, N. P., and Cava, R. J. Anisotropic properties of the layered superconductor Cu_{0.07}TiSe₂. *Phys. Rev. B* **75**(10), 104505, (2007).
 - [12] Li, S. Y., Wu, G., Chen, X. H., and Taillefer, L. Single-gap s-wave superconductivity near the charge-density-wave quantum critical point in Cu_xTiSe₂. *Phys. Rev. Lett.* **99**(10), 107001 (2007).
 - [13] Jishi, R. A. and Alyahyaei, H. M. Electronic structure of superconducting copper intercalated

- transition metal dichalcogenides: First-principles calculations. *Phys. Rev. B* **78**(14), 144516 (2008).
- [14] Di Salvo, F. J., Moncton, D. E., and Waszczak, J. V. Electronic properties and superlattice formation in the semimetal TiSe_2 . *Phys. Rev. B* **14**(10), 4321–4328, Nov (1976).
 - [15] Li, G., Hu, W. Z., Qian, D., Hsieh, D., Hasan, M. Z., Morosan, E., Cava, R. J., and Wang, N. L. Semimetal-to-semimetal charge density wave transition in 1T- TiSe_2 . *Phys. Rev. Lett.* **99**(2), 027404 (2007).
 - [16] Wilson, J. A. Concerning the semimetallic characters of TiS_2 and TiSe_2 . *Solid State Comm.* **22**(9), 551–553, June (1977).
 - [17] Kidd, T. E., Miller, T., Chou, M. Y., and Chiang, T.-C. Electron-hole coupling and the charge density wave transition in TiSe_2 . *Phys. Rev. Lett.* **88**(22), 226402, May (2002).
 - [18] Rossnagel, K., Kipp, L., and Skibowski, M. Charge-density-wave phase transition in 1T- TiSe_2 : Excitonic insulator versus band-type Jahn-Teller mechanism. *Phys. Rev. B* **65**(23), 235101, May (2002).
 - [19] Hughes, H. P. Structural distortion in TiSe_2 and related materials - a possible Jahn-Teller effect? *J. Phys. C: Solid State Phys.* **10**(11), L319–L323 (1977).
 - [20] Whangbo, M. H. and Canadell, E. Analogies between the concepts of molecular chemistry and solid-state physics concerning structural instabilities. electronic origin of the structural modulations in layered transition metal dichalcogenides. *J. Am. Chem. Soc.* **114**(24), 9587–9600 (1992).
 - [21] Suzuki, N., Yamamoto, A., and Motizuki, K. Microscopic theory of the CDW State of 1T- TiSe_2 . *J. Phys. Soc. Jpn.* **54**, 4668 (1985).
 - [22] Motizuki, K., Suzuki, N., Yoshida, Y., and Takaoka, Y. Role of electron-lattice interaction in lattice dynamics and lattice instability of 1T- TiSe_2 . *Solid State Communications* **40**(11), 995 – 998 (1981).
 - [23] Zunger, A. and Freeman, A. J. Band structure and lattice instability of TiSe_2 . *Phys. Rev. B* **17**(4), 1839–1842, Feb (1978).
 - [24] Cercellier, H., Monney, C., Clerc, F., Battaglia, C., Despont, L., Garnier, M. G., Beck, H., Aebi, P., Patthey, L., Berger, H., and Forró, L. Evidence for an Excitonic Insulator Phase in 1T- TiSe_2 . *Phys. Rev. Lett.* **99**(14), 146403 (2007).
 - [25] Monney, C., Cercellier, H., Clerc, F., Battaglia, C., Schwier, E. F., Didiot, C., Garnier, M. G.,

- Beck, H., Aebi, P., Berger, H., Forro, L., and Patthey, L. Spontaneous exciton condensation in 1T-TiSe₂: BCS-like approach. *Phys. Rev. B* **79**(4), 045116 (2009).
- [26] Monney, C., Cercellier, H., Clerc, F., Battaglia, C., Schwier, E. F., Didiot, C., Garnier, M. G., Beck, H., and Aebi, P. Temperature dependence of the excitonic insulator phase model in 1T-TiSe₂. *arXiv:0809.1936v1[cond-mat.str-el]* (2008).
- [27] Holt, M., Zschack, P., Hong, H., Chou, M. Y., and Chiang, T.-C. X-Ray Studies of Phonon Softening in TiSe₂. *Phys. Rev. Lett.* **86**(17), 3799–3802, Apr (2001).
- [28] Voit, J., Perfetti, L., Zwick, F., Berger, H., Margaritondo, G., Gruner, G., Hochst, H., and Gri-
oni, M. Electronic Structure of Solids with Competing Periodic Potentials. *Science* **290**(5491),
501–503 (2000).
- [29] van Wezel, J., Nahai-Williamson, P., and Saxena S.S. Accepted for publication.
- [30] van Wezel, J., Nahai-Williamson, P., and Saxena S.S. To be published.
- [31] Varma, C.M., Schmitt-Rink, S., and Abrahams, E. Charge transfer excitations and supercon-
ductivity in 'ionic' metals. *Solid State Comm.* **62**(10), 681–685 (1987).
- [32] Littlewood, P.B. Collective modes and superconductivity in an extended Hubbard model for
copper oxide superconductors. *Phys. Rev. B* **42**(16), 10075–10089 (1990).
- [33] Nakai, N., Ichioka, M., and Machida, K. Field dependence of electronic specific heat in two-
band superconductors. *J. Phys. Soc. Japan* **71**(1), 23–26, January (2002).
- [34] Kiss, T., Yokoya, T., Chainani, A., Shin, S., Hanaguri, T., Nohara, M., and Takagi, H.
Charge-order-maximized momentum-dependent superconductivity. *Nat. Phys.* **3**(10), 720–
725, October (2007).
- [35] Slater, J. C. and Koster, G. F. Simplified LCAO Method for the Periodic Potential Problem.
Phys. Rev. **94**(6), 1498–1524, Jun (1954).
- [36] Harrison, W. *Electronic structure and the properties of solids*. Freeman, San Francisco, (1989).
- [37] Yoshida, Y. and Motizuki, K. Electron Lattice Interaction and Lattice Instability of 1T-TiSe₂.
J. Phys. Soc. Jpn. **49**(3), 898–905 (1980).